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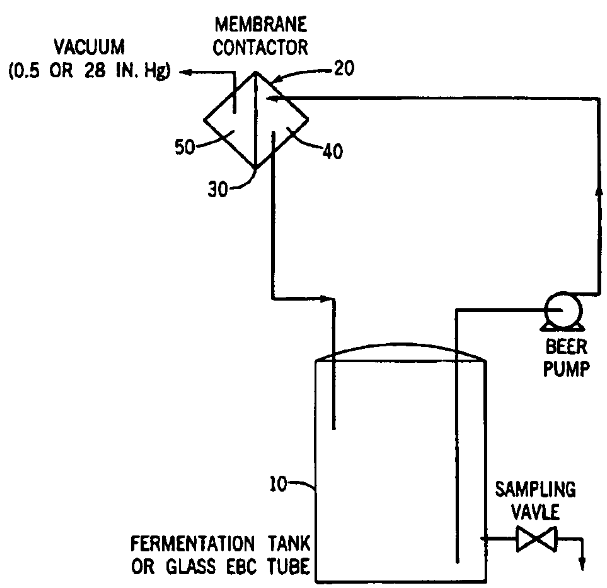
(54) Title: METHOD OF REMOVING CARBON DIOXIDE FROM FERMENTING MEDIUM USING A POLYMERIC MEMBRANE



(57) Abstract: Disclosed is a method for removing carbon dioxide from fermenting medium. The method includes the steps of transferring a portion of the fermenting beer to a membrane contactor comprising at least one polymeric membrane having a gas side and a liquid side, wherein carbon dioxide present in the wort transfers from the liquid side of the membrane to the gas side of the membrane.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

METHOD OF REMOVING CARBON DIOXIDE FROM FERMENTING MEDIUM USING A POLYMERIC MEMBRANE

CROSS-REFERENCE TO RELATED APPLICATIONS

Not applicable

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

Not applicable.

BACKGROUND OF THE INVENTION

The buildup of carbon dioxide (CO_2) formed during brewing and other alcoholic fermentations is associated with a number of disadvantages. The CO_2 generated during conventional fermentations first saturates the fermenting medium and then forms gas bubbles, which rise to the headspace of the fermenter, causing the formation of foam.

Foam production is undesirable for a several reasons. Foam formed during lager or ale fermentations may occupy as much as one third of the fermenter volume. If insufficient headspace is allowed, overfoaming of the fermenter can occur, resulting in product loss, environmental problems, increased BOD load, sanitation problems, loss of collectable CO_2, and increased manpower requirements.

The large headspace required to avoid overfoaming severely limits fermenter capacity utilization. Maximizing fermenter capacity is an important goal within the brewing industry, because increased fermenter capacity reduces the cost of production. Brewers have attempted to increase production capacity by increasing the gravity of the wort or increasing fermentation temperatures. Unfortunately, both of these modifications cause increased foam formation;

the increased headspace required to avoid overfoaming partially offsets the potential capacity increase.

Several methods to reduce foaming have been investigated or employed by brewers. One method that has been used is adding anti-foaming agents to the beer during fermentation to reduce foaming. Such agents, which are often based on poly-dimethyl-siloxane, are not always acceptable to brewers, because the agents may be considered additives. Another foam reduction method employs a mechanical foam breaker such as a cyclone to reduce foaming. Ultrasonic foam breakers placed in the top of fermenters have also been used to reduce foaming.

Although the aforementioned methods reduce foam, some foam remains. In general, these methods destroy foam after it has formed, which results in the loss of certain desirable hydrophobic substances that tend to concentrate in the foam, including hop bitter acids and high molecular weight proteins responsible for a good head in the final product. After foam collapse, these substances may precipitate and not go back into solution. Preventing the formation of foam will prevent the loss of these components.

Foam is formed after CO_2 bubbles that are generated in the fermenting medium rise to the top and become surrounded by a thin liquid film containing surface-active materials. Carbon dioxide bubbles are formed at nucleation centers in the fermenting medium at points where the dissolved CO_2 concentration exceeds the local equilibrium partial pressure.

Another problem associated with the buildup of CO_2 during fermentation is that high concentrations of CO_2 alter or inhibit yeast metabolism. For example, high levels of CO_2 found in fermenting wort cause a reduction in yeast production of esters, important components in the flavor and aroma of beer. Absent a means for regulating

the CO_2, the concentration of CO_2 in fermenting medium varies greatly according to the fermenter size and geometry. Therefore, beer flavor profiles are also affected by the type of fermenter used.

In conventional brewing methods, agitation of the fermentation medium is provided by the evolution of CO_2 bubbles. Agitation is important in the brewing process, because the level of agitation is directly related to the fermentation rate. The level of agitation depends on formation of CO_2 gas bubbles; therefore, it follows that systems in which CO_2 bubbling is not regulated do not permit control of agitation. Because the rate of bubble formation is affected by fermenter geometry and size, agitation and fermentation rates in conventional brewing systems will vary from fermenter to fermenter. This makes it difficult to achieve consistency between fermentations conducted in fermenters of different sizes or geometries.

Carbon dioxide produced during fermentation may be collected and used in other commercially important applications, such as carbonating beverages. In conventional methods, CO_2 is used to sweep out the headspace to eliminate unwanted oxygen prior to collecting CO_2. This results in a loss of about 10% of collectable CO_2.

What is needed in the art is a method of removing CO_2 from fermentation media during fermentation so as to increase capacity, provide greater flexibility by the ability to control agitation independent of bubble formation, produce more consistent flavor profiles, and recover more high quality CO_2. As shown in the examples, fermentations in which nonaerated wort was pitched with yeast oxygenated by the method of the invention

BRIEF SUMMARY OF THE INVENTION

The present invention provides a method for removing CO_2 from a fermenting liquid medium, comprising the steps of: transferring at least a portion of the fermenting medium through a membrane contactor, the contactor comprising at least one polymeric membrane, the membrane having a liquid side and a gas side, wherein at least a portion of the medium is in proximity to the liquid side of the membrane under conditions that allow CO_2 in the medium to transfer from the liquid side of the membrane to the gas side of the membrane.

It is an object of the present invention to provide a method of removing CO_2 from fermenting medium.

Another object of the invention is to prevent the formation of foam during fermentation.

It is a further object of the invention to remove CO_2 formed during fermentation to permit greater flexibility in developing beers with different flavor profiles.

It is an advantage that the invention provides a method that will allow increased capacity utilization.

It is a further advantage that the method of the invention essentially eliminates foam formation, thereby preventing the loss of desired beer components.

An additional advantage of the method is that it allows the possibility of controlling CO_2 levels and agitation independently.

Another advantage of the invention is that a greater percentage of collectable CO_2 produced during fermentation may be collected as high quality CO_2.

The method of the invention is advantageous in that it provides a method of controlling the amount of CO_2 present during fermentation, rendering the beer flavor profiles independent of fermenter size or geometry.

Other objects, features and advantages of the present invention will become apparent upon review of the

specification.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

Fig. 1 shows a circulating system for removing CO_2 from fermenting liquid medium employing a polymeric membrane contactor.

DETAILED DESCRIPTION OF THE INVENTION

The buildup of CO_2 during wort fermentation reduces capacity utilization; causes foaming, which reduces the concentration of desired components in beer; and affects beer flavor profiles in a way that imposes constraints on the size and geometry of fermenters that can be used for brewing certain types of beer.

The present invention includes a method of removing CO_2 from a fermenting liquid medium so as to prevent foam formation, increase capacity utilization, reduce the loss of desired components during fermentation, decouple agitation rate from the rate of CO_2 formation, permit control of CO_2 levels, allow recovery of higher quality CO_2, allow greater recovery of recoverable CO_2, and allow greater flexibility in brewing by controlling CO_2 levels regardless of fermenter size or geometry.

By a fermenting liquid medium, it is meant a liquid medium comprising a fermentable carbon source and a microorganism that ferments the carbon source, producing CO_2 as a byproduct. Preferably, the microorganism is yeast.

In the method of the invention, CO_2 is removed from a fermenting liquid medium by passing a portion of the medium through a membrane contactor comprising at least one polymeric membrane comprising a liquid side and a gas side, such that the transferred medium is in proximity with the liquid side of the membrane and CO_2 is transferred from the medium to gas side of the membrane.

Preferably, the partial pressure of CO_2 is maintained at a lower level on the gas side of the membrane than the CO_2 partial pressure in the head space of the fermenter. This may be done by application of a vacuum. Alternatively, CO_2 may be removed by flushing with a suitable gas, such as nitrogen.

As described in the examples and as shown in Fig. 1, the CO_2 may be removed from fermenting liquid medium according to the method of the invention by recirculating a portion of the fermenting medium through a CO_2 removal system. Removal of CO_2 from fermenting liquid medium in a fermenter **10** is accomplished by transferring a portion of the medium from the fermenter **10** to a membrane contactor **20**, the contactor **20** comprising a microporous hydrophobic membrane or a nonporous hydrophobic or hydrophilic membrane **30**, the membrane having a liquid side **40** and a gas side **50**. Carbon dioxide in the medium passes from the liquid side **40** of the membrane **40** to the gas side **50** of the membrane **30**. Carbon dioxide removal from the gas side **50** of the membrane **30** is facilitated by maintaining the partial pressure of CO_2 on the gas side lower than the CO_2 partial pressure of the head space in the fermenter. This may be accomplished by the application of a vacuum from a vacuum source or by flushing with a gas supplied by a gas source. Optionally, CO_2 stripped from the membrane may be collected in a CO_2 collector. Following CO_2 removal in the membrane contactor **20**, the medium is returned to the fermenter **10**. Preferably, recirculation of the medium is conducted in a continuous process. In an alternative embodiment, the membrane contactor may be housed within the fermentation tank.

As described in the examples, CO_2 was removed from wort using a polymeric hollow fiber membrane across which gas may be exchanged. A membrane provides a high surface

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area contact with the liquid wort. A high ratio of membrane surface area to wort volume provides a high specific area for mass transfer.

As described in the examples below, the method of the invention was evaluated using a hydrophobic membrane of the type used as a blood oxygenator (Model Max-FTE, Medtronic, Minneapolis, MN). A mass transfer devise of the type used in the examples is described in detail in U.S. Patent 4,975,247, which is incorporated by reference. In the examples, the membrane contactor was equipped with a plurality of microporous, hydrophobic hollow fiber membranes made from polypropylene, with a pore size of about 0.03 um and a porosity of about 40%.

Examples of suitable hydrophobic membranes include, but are not limited to polysulfone, polytetrafluoroethylene (PTFE or Teflon), polyvinylidenefluoride, polyvinylidenechloride, and polyethylene. A nonporous hydrophobic or hydrophilic membrane may also be used in the present invention. With nonporous membranes, the rate of transfer of CO_2 from the liquid to the gas side will depend on the rate of diffusion through the nonporous membrane. However, it is reasonably expected that acceptable rates of CO_2 removal may be obtained using nonporous membranes.

One skilled in the art will appreciate that in addition to the membrane contactor disclosed in the examples, there are other membrane configurations that are also suitable for use in the invention. It is expected that spiral wound, vibrating, rotary and tubular hollow fiber membranes may also be used in the practice of the invention. The membrane contactor used in the examples is suitable for relatively small fermentation volumes. One of skill in the art would appreciate that for relatively large fermentations, one would wish to use a larger contactor.

Optionally, volatile compounds from the CO_2 gas stream may be collected and used in other applications. For example, the CO_2 present in the gas stream could be trapped using a cold trap placed between the membrane contactor and the vacuum source. Alternatively, CO_2 could be absorbed using a suitable liquid or selectively adsorbed by solid adsorbents. Preferably, the oxygen concentration in the CO_2 recovered from the fermentation is less than about 50 ppm. Still more preferably, the oxygen concentration in the CO_2 recovered from the fermentation is less than about 25 ppm or even as low as 5 ppm or less.

The method of the invention allows relatively high recovery of recoverably CO_2 generated during fermentation because it eliminates the loss of CO_2 that occur during conventional venting. Preferably, 95% or even as much as 99% or greater recovery of recoverable CO_2 is achieved by this method. The initial concentration of oxygen is relatively low because the fermenter is filled to a greater capacity than is possible in conventional methods. To reduce contamination of CO_2 with oxygen, CO_2 removal is preferably begun after yeast in the fermenter have taken up essentially all of the oxygen in the medium. In general, oxygen uptake is essentially completed from about 0 to 6 hours after pitching, depending on a variety of factors, including pitching rate.

In order to afford greater consistency between fermentations or to achieve certain flavor profiles, one may wish to monitor and control removal of CO_2 over the course of the fermentation. Carbon dioxide may be monitored by sampling the fermentation medium and measuring its CO_2 content. Levels of CO_2 may be controlled most suitably by controlling the partial pressure of CO_2 on the gas side of the membrane or by adjusting the flow rate of the liquid medium. Partial pressure of CO_2 on the gas side may be controlled by application of a vacuum, or by

flushing with a suitable gas, such as nitrogen.

By the method of the invention, the capacity utilization is increased dramatically relative to that achievable using conventional venting. By "conventional venting" is meant releasing CO_2 from the headspace to the atmosphere or to a CO_2 collection system. It is reasonably expected that tanks may be filled to 80%, 90%, 95%, or even as high as 99% or greater capacity without overfoaming. The method of the invention is expected to allow high capacity utilization, even when the specific gravity of the medium or the temperature of fermentation is increased.

Conventional fermentations depend on the generation of CO_2 to achieve agitation. The rate of fermentation is directly related to the degree of agitation. However, high concentrations of CO_2 interfere with yeast metabolism. The method of the invention decouples CO_2 generation and agitation rates.

In the examples, agitation is achieved by recirculating the fermentation medium between the fermenter and the membrane contactor. However, one could further increase agitation by including a mechanical agitator, such as a motorized impeller.

In the examples, the medium was recirculated between the contactor and fermenter at a rate of 800 ml/min. The residence time of the wort in the contactor was about 9 seconds. The average velocity was about 41 cm/min in the fiber bed, and the superficial velocity (flow rate/cross sectional area of the fiber bed) was about 13.7 cm/min. One of ordinary skill in the art will appreciate that one may vary these parameters and still achieve acceptable carbon dioxide removal, provided that the K_La value is high. Preferably, the K_La value is in the range of from about 0.05 sec^{-1} to about 0.4 sec^{-1}.

Using the method of the invention, foam formation

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during fermentation is essentially eliminated. However, we expect that the method of the invention may be useful in applications in which foam formation is reduced but not eliminated. Therefore the present invention is not intended to be limited to conditions in which foam formation is eliminated.

Because hop acids and beer foam proteins are lost when beer foam formed during fermentation collapses, it is reasonably expected that a beer made by the process of the invention will retain higher concentrations of hop acids or beer foam proteins than a control beer made by the same process without removing CO_2 formed during fermentation.

In the examples described below, the flow path of the liquid medium within the a hollow membrane fiber was in a dirction substantially perpendicular to the fiber axis (cross flow). It is expected that parallel and counter current flows may also be successfully employed. Although a method employing cross flow is likely to give better results, parallel flow is also expected to be suitable for use in the method of the invention.

The following nonlimiting examples are intended to be purely illustrative.

Materials

For the CO_2 removal experiments described below, fermentations were conducted in volumes of 2 and 20 liters using wort having an original gravity of about 15 degrees Plato pitched at a rate of about 0.8 g yeast dry weight/liter wort.

The membrane contacter employed in the CO_2 removal studies (Model MAX-FTE, Medtronic, Minneapolis, MN) was equipped with a standard polypropolyene microporous membrane having a surface area of about 2.4 m^2 and a liquid hold-up volume of about 120 ml.

Bubble-free CO_2 removal during fermentation

The method by which CO_2 was removed from fermenting liquid medium is shown schematically in Figure 1. Pitched wort was contained in a 26 L stainless steel tank equipped with a magnetic stir bar for continuous mixing and a temperature control system for maintaining the fermenting wort at a predetermined temperature. The yeast was allowed assimilate oxygen for a period of 3 hours after pitching. A membrane contactor that had been purged with ambient pressure CO_2 to remove essentially all traces of atmospheric oxygen was then connected to the fermenter. A portion of the fermenting wort was pumped to the membrane contactor at a flow rate of about 800 ml/min. The residence time of the wort in the contactor was about 9 seconds. The average velocity of was about 41 cm/min in the fiber bed, and the superficial velocity (flow rate/cross sectional area of the fiber bed) was about 13.7 cm/min. Carbon dioxide present in the wort was transferred from the liquid side to the gas side of the membrane contactor, which was connected to a regulated vacuum source.

Periodically, liquid samples from the fermenter were collected to monitor cell growth, extract consumption, and pH.

Foaming potential was visualized using the above-described membrane and vacuum set up using a glass tube (50 mm ID x 2 m long) as the fermenter in place of the stainless steel tank. Essentially no foam was generated in a system comprising the membrane contactor coupled with vacuum application, relative to a control fermentation in which CO_2 removal was accomplished by conventional venting, or a control fermentation undergoing conventional venting and recirculation at the same rate as the test. The liquid recirculation rates used in the fermentations were 800 mL/min regardless of fermentation volume (2 L or 20 L of

fermenting wort). Vacuum levels of 0.5 inches (14.45 psia) to 28 inches (0.9 psia) of mercury were employed. No foam was generated during fermentations employing the contactor membrane system, even using a vacuum level as low as 0.5 inches of mercury.

The present invention is not limited to the exemplified embodiment, but is intended to encompass all such modifications and variations as come within the scope of the following claims.

CLAIMS

WE CLAIM:

1. A method of removing carbon dioxide from a fermenting liquid medium comprising the step of:
(a) transferring a portion of the medium to a membrane contactor comprising at least one polymeric membrane having a liquid side and a gas side, wherein the medium is in proximity to the liquid side of the membrane, under conditions that allow at least a portion of the carbon dioxide present in the medium to transfer from the liquid side to the gas side of the membrane.

2. The method of claim 1, further comprising the step of:
(b) after step (a), removing carbon dioxide from the contactor by maintaining a partial pressure of carbon dioxide on the gas side lower than the partial pressure of carbon dioxide in the headspace.

3. The method of claim 2, wherein the partial pressure of CO_2 on gas side of the membrane is maintained by applying a vacuum to the gas side.

4. The method of claim 2, wherein the partial pressure of carbon dioxide on gas side of the membrane is maintained by flushing the gas side of the membrane with a suitable gas.

5. The method of claim 1, wherein the carbon dioxide removed from the medium is collected.

6. The method of claim 5, wherein the recovered carbon dioxide has less than 50 ppm O_2.

7. The method of claim 5, wherein the carbon dioxide has less than 5 ppm O_2

8. The method of claim 1, wherein the medium is recirculated between the fermenter and the membrane contactor.

9. The method of claim 1, wherein the carbon dioxide concentration in the medium is controlled during fermentation.

10. The method of claim 1, wherein the fermenter capacity utilization is increased relative to a control process in which the carbon dioxide is removed by conventional venting.

11. The method of claim 5, wherein the carbon dioxide collected is higher than carbon dioxide collected in a control process in which the carbon dioxide is removed by conventional venting.

12. A method of producing a fermented beverage, wherein carbon dioxide formed during fermentation is removed according to the method of claim 1.

13: The method of claim 12, wherein the fermented beverage is beer.

14. The method of claim 12, wherein the carbon dioxide concentration in the medium is controlled during fermentation.

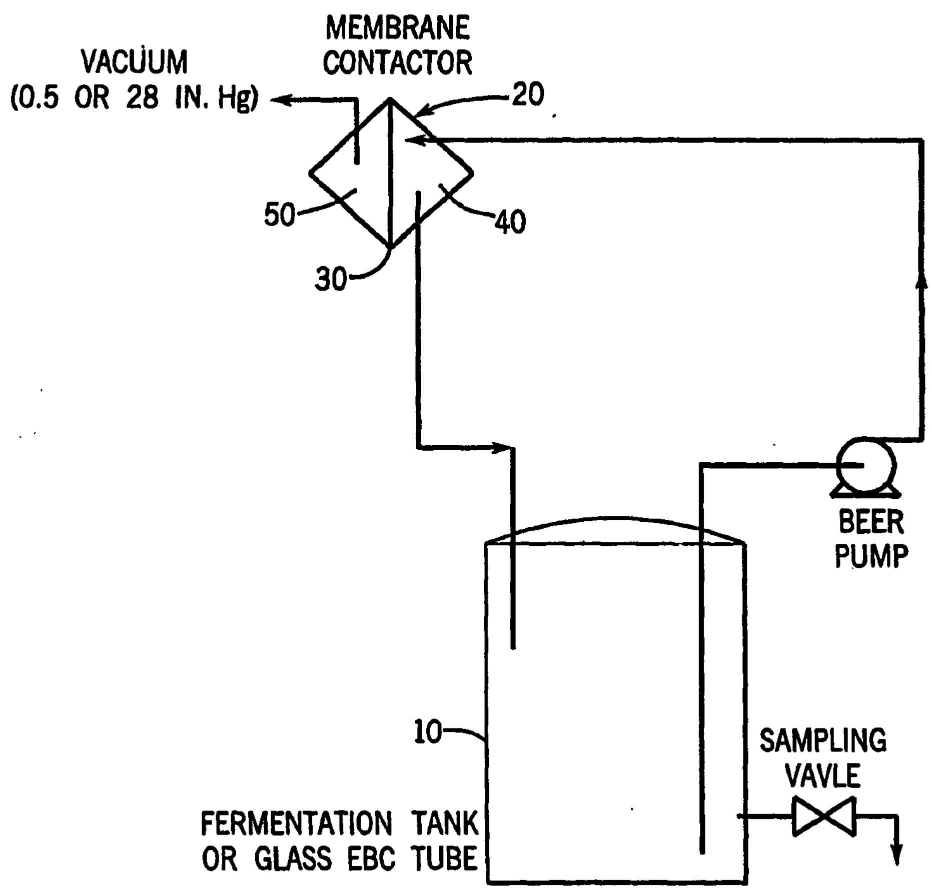
15. The process of claim 12, wherein fermentation is conducted in a fermenter, and wherein fermenter capacity utilization is increased relative to a control process in which the carbon dioxide is removed by conventional venting.

16. The process of claim 12, wherein the agitation rate is decoupled from the generation of carbon dioxide.

17. A beer produced by the method of claim 12.

18. The beer of claim 17, wherein the beer has a greater concentration of at least one component selected from the group consisting of bitter acids and high molecular weight foam proteins relative to a beer made by a comparable method lacking the carbon dioxide removal step in which carbon dioxide is vented by a conventional method.

FIG. 1


MEMBRANE
CONTACTOR
VACUUM
(0.5 OR 28 IN. Hg)
20
50
40
30
BEER
PUMP
10
SAMPLING
VAVLE
FERMENTATION TANK
OR GLASS EBC TUBE

INTERNATIONAL SEARCH REPORT

I ational Application No
PCT/US 00/27571

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C12C11/04 C12F3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C12C C12F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 565 149 A (PAGE JOHN K R ET AL) 15 October 1996 (1996-10-15) column 8, line 38-54; figure 3 column 9, paragraph 1 column 17, line 45-56 column 18, line 9-33; claim 1	1-3, 8-10, 12-15,17
A		4,11,16, 18
X	US 3 769 176 A (HISE R ET AL) 30 October 1973 (1973-10-30) column 3, line 2-21; figure 2 column 5, line 53-61 claims 1,11,13	1,5

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 February 2001	14/02/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rooney, K

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 770 455 A (VAN GHELUWE J ET AL) 6 November 1973 (1973-11-06) claim 1	6,7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/27571

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